was treated with 27 g (0.25 mole) of chlorotrimethylsilane at 25°. No temperature rise was observed, and after 48 hr the reaction mixture remained unchanged.

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Reaction of Butadiene with Ethylene. II.[1] New Catalytic Systems in Synthesis of 1,4-Hexadiene

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1,4-Hexadiene is of commercial interest because of its utility as the third monomer for sulfur-curable ethylene propylene rubber. Recently, the preparation of the diene by a catalytic reaction of butadiene with ethylene has been reported by Hata[2] and by Alderson, *et al.*[3] Thermally initiated reaction of acetylene with 1-butene also yielded the diene.[4] The present work was undertaken in order to explore catalysts for the synthesis of 1,4-hexadiene from butadiene and ethylene. We have found that the catalytic systems consisting of an iron halide, an organoaluminum compound, and a ditertiary phosphine exert excellent selectivity in the formation of the diene.

Among the effective organoaluminum compounds are triethylaluminum, triisobutylaluminum, diisobutylaluminum hydride, and diethylaluminum chloride. As an iron halide component, ferric chloride and ferric bromide are suitable. Some ditertiary phosphines are used as the third component in these systems and it is considered that the phosphines affect the conversion and the selectivity of 1,4-hexadiene. Bis(diphenylphosphino)ethane, bis(diphenylphosphino)propane, bis(diphenylphosphino)ethylene (*cis* and *trans* isomers), and *o*-phenylenebis(diphenylphosphine) were found to be effective as the third component. The catalysts were prepared by mixing the three components in a solvent in an inert atmosphere. According to the results shown in Table I, the effectiveness of each component was in the following order: organoaluminum compound, $(C_2H_5)_3Al > (i\text{-}C_4H_9)_3Al > (i\text{-}C_4H_9)_2AlH > (C_2H_5)_2AlCl$; iron halide, $FeCl_3 > FeBr_3 > FeI_2$; ditertiary phosphine,[5] DPP ≥ DPE > *cis*-DPET > *trans*-DPET > PDP > DPM.

In the system containing triethylaluminum, ferric chloride, and DPE, the amount of nondistillable material (shown as residue in Table I) tended to increase and the selectivity of 1,4-hexadiene tended to decrease as the charged butadiene increased. A high conversion based on the charged butadiene was obtained at 80 to 100°. The molar ratio of the phosphine to ferric chloride remarkably affected the process. The proper ratio was within the limits of 0.5 to 1.

Chatt and Hayter[6] have prepared the complex of $[FeCl_2(\text{diphosphine})_2][FeCl_4]$ type from an equimolar mixture of ferric chloride and diphosphine. Then the complex has been reduced with lithium aluminum hydride to give $FeH_2(\text{diphosphine})_2$ in a minor yield. It is not clear whether the definite complex such as that obtained by Chatt and Hayter was formed or not in the ternary systems of this work. Ferric chloride is obviously reduced with triethylaluminum to a lower valent species. Simultaneously, diphosphine coordinates to the lower valent iron atom as a chelate ligand and stabilizes the catalytically active iron complex by forming a dative π bond between the iron atom and phosphorus atom.[7] As it blocks at least two of the coordination positions on the iron atom, the reactants approaching the iron atom, that is the catalytic site, should be limited and orientated.

The formation of 1,4-hexadiene must involve a hydrogen shift from ethylene to butadiene. In a linear dimerization of butadiene, the hydrogen shift *via* metal–hydrogen bonding has been assumed by Otsuka.[8] Cobalt and iron compounds, especially as carbonyl and hydridocarbonyl compounds, are used as hydrogen carrier.[9] These facts and the formation of iron hydrido complex described previously suggest some postulates on the reaction mechanism. One of them is as follows: an iron hydridodiphosphine complex is formed by the reaction of the catalyst components and the complex reacts with butadiene to give π-butenyl complex such as the complex derived from butadiene and hydridocobalt tetracarbonyl.[10] One hydrogen atom of the coordinated ethylene is pulled out by the iron atom of the complex and the residual group of the ethylene molecule simultaneously attacks the π-allyl part of the butenyl group, then 1,4-hexadiene leaves the catalytic site and the hydridodiphosphine complex is regenerated. An alternate postulate is as follows: the iron hydrido complex reacts with butadiene to give σ-butenyl complex and after ethylene coordinates with the complex, the butenyl group adds to the ethylene to form a σ-hexenyliron complex. This complex then disproportionates to give 1,4-hexadiene and the iron hydrido complex. The fact that butadiene and ethylene react so easily by means of these iron catalyst is strong evidence for a coordination mechanism. 3-Methyl-1,4-pentadiene is one of the possible products in the former mechanism, but it was not detected in any

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TABLE I

REACTIONS OF BUTADIENE WITH ETHYLENE[a]

Run no.	Iron halide, mmoles	Phosphine, mmoles	Organoaluminum compound,[b] mmoles	Butadiene, g	Reaction conditions Pressure, kg/cm²	Temperature, °C	Time, hr	Products, g 1,4-HD[c]	2,4-HD[c]	Residue	Conversion,[d] %	Selectivity,[e] %
1	2	DPE, 1	TEA, 7.3	67	70	50	5	35.7	...	7.2	42.9	82.7
2	2	DPE, 1	TEA, 7.3	67	60	80	3	69.5	1.5	10.4	86.6	80.6
3	2	DPE, 0.1	TEA, 7.3	100	60	80	18	51.3	1	41.4	76	45
4	1	DPE, 0.5	TEA, 7.3	100	60	80	18	35.4	1	13.3	37.5	62.8
5	1	DPE, 1	TEA, 7.3	100	60	80	18	95.5	2.3	13.1	78.2	81.1
6	5	DPE, 1	TEA, 7.3	100	60	80	18	92.8	2.5	10.4	74	83.7
7	0.1	DPE, 1	TEA, 7.3	67	60	80	3	3.2	...	2.8	7.4	...
8	2	DPE, 1	TEA, 7.3	20	68	80	2	24.6	0.2	2	86.6	95
9	2	DPE, 1	TIBA, 4	67	65	80	2	78.6	1.2	7.2	90.6	86.8
10	2	DPE, 1	DIBAH, 5.6	67	65	80	2	61.5	...	8.1	73.4	83.5
11	2	DPE, 1	DEAC, 8	67	65	80	2	18.9	...	2.7	24.4	82.4
12	0.5	DPM, 1	TEA, 7.3	67	60	85	2	2.5	...	26.7	42.3	...
13	0.5	DPP, 1	TEA, 7.3	67	60	85	3	96	...	2.6	100	96.2
14	0.5	PDP, 1	TEA, 7.3	67	60	85	3	29.3	...	22.3	62.5	...
15	2	*cis*-DPET, 1	TEA, 7.3	67	50	85	3	64.3	2	26	97.3	66
16	2	*trans*-DPET, 1	TEA, 7.3	67	50	85	3	40	...	10.4	55.3	72
17	0.5	DPE, 0.5	TOA, 7.3	67	40	80	17	79.3	...	7.6	90.5	87.2
18	0.7	DPE, 0.5	TEA, 16	40	40	80	3	11.2	...	2.5	24.6	76.6

[a] Twenty milliliters of monochlorobenzene was used through all runs. Runs 1–16 ferric chloride; 17, ferric bromide; and 18, ferrous iodide. [b] TEA = triethylaluminum, TIBA = triisobutylaluminum, DIBAH = diisobutylaluminum hydride, DEAC = diethylaluminum chloride. [c] HD = hexadiene. [d] Moles of butadiene reacted/moles of butadiene charged × 100. [e] Moles of 1,4-hexadiene formed/moles of butadiene reacted × 100.

runs. In case monodentate triphenylphosphine was added to the catalytic system instead of ditertiary phosphine, 1,4-hexadiene, 3-methyl-1,4-pentadiene, and 1,3-hexadiene were prepared.[1] Therefore, it is considered that a coordination of the ditertiary phosphine governs the reaction of π-butenyl group with the coordinated ethylene to form exclusively 1,4-hexadiene. The exclusive formation of *cis* isomer may be a clue to make clear the reaction mechanism, however, further study will be required to elucidate the detail.

Experimental Section

Materials.—Anhydrous ferric chloride was purified by sublimation before use. Ferric bromide and ferrous iodide of extra pure grade were used without further purification. Organoaluminum compounds were obtained commercially. Monochlorobenzene was dried with phosphorus pentoxide and subsequently distilled. Ditertiary phosphines were prepared according to the method of Hewertson and Watson.[11]

Reaction of Butadiene with Ethylene.—In a typical example, 2 mmoles of ferric chloride, 1 mmole of DPE, 20 g of liquefied butadiene, and 7.3 mmoles of triethylaluminum were added in that order into 80 ml of monochlorobenzene in a stainless steel autoclave (200 ml) equipped with a magnetic stirrer. After the autoclave was tightly closed, ethylene was introduced directly from a cylinder up to 68 kg/cm² at 80°. The reaction was carried out for 2 hr under a constant pressure and temperature. By adding a small amount of dilute hydrochloric acid in a separatory funnel. The upper layer was washed thoroughly with water and dried with anhydrous sodium sulfate. Then the atmospheric distillation was carried out and the distillate was analyzed by gas chromatography (Apiezon grease L packing column 3 m, carrier gas helium, 100°). The yield was calculated from the relative peak area in comparison with the peak area of toluene added as an internal standard. The validity was confirmed by the analysis of known mixtures. In the example, the yield of 1,4-hexadiene was 24.6 g, and 0.2 g of 2,4 isomer and 2 g of nondistillable material were also obtained. 1,4-Hexadiene and 2,4-hexadiene were purified by preparative gas chromatography, and were identified by elementary analysis, infrared absorption spectroscopy, mass spectroscopy, and gas chromatography.

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The Ultraviolet Spectrum of Allylmercuric Iodide and Its Acid Cleavage Mechanism[1a]

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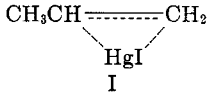
Allylmercuric iodide is cleaved by acid some six powers of 10 faster than propene is hydrated, in spite of the fact that both of them involve the attack of the proton on the methylene group of the carbon–carbon double bond.[2,3] This requires that considerable electron density be transferred, in the transition state, from the mercury to the carbon acquiring the formal positive charge. An attractive way to accomplish this would be to have a transition state resembling the olefin–mercuric iodide π complex (I) in its electronic structure. Kinetic isotope effects, however, require that the reaction coordinate *not* contain large components of heavy atom motions.[2] Therefore, a structure similar to I in its heavy-atom geometry would either have to be formed in the activation process or would have to be already present in the starting state. It is the purpose of the present note to suggest, on the basis of ultraviolet spectra, that the latter



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[1] (a) Supported, in part, by the National Science Foundation through GP-5088; (b) National Science Foundation Cooperative Graduate Fellow, 1963–1965.

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